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PREDICTION OF HYDROGEN ENTRY AND PERMEATION IN METALS AND ALLOYS

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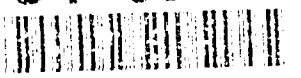

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13. ABSTRACT (Maximum 200 words)

This Grant focused on the investigation of the factors which affect hydrogen entry and permeation into metals/alloys that by themselves or in combination with other materials are used under conditions for which hydrogen embrittlement and cracking are a major concern.

Factors that affect H entry include a broad range of metallurgical, environmental and interface properties such as adsorption, surface segregation, surface films and recesses in the surface. Research during this grant period focused on understanding how these parameters control hydrogen entry. The specific investigations included both aqueous and gas phase charging of hydrogen, utilizing primarily electrochemical techniques, in particular hydrogen permeation with the IPZ model, and microscopic methods in the case of aqueous phase charging, and ultra high resolution scanning tunneling microscopy (STM) in the case of gas phase charging.

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RESEARCH GOALS

This Grant focused on the investigation of the factors which affect hydrogen entry and permeation into metals/alloys that by themselves or in combination with other materials are used under conditions for which hydrogen embrittlement and cracking are a major concern. Hydrogen entry is the first step in the severe hydrogen degradation of the mechanical properties of structural alloys. Hydrogen entry occurs during the cathodic protection of structures, during corrosion processes, and during the processing of steels for which the source can be either the aqueous phase, e.g., as in electrogalvanizing of steel, or the gas phase. Once hydrogen is inside the material in solid solution or as hydride, loss of structural integrity can occur at any time during the service application to produce the so called "delayed failure". Factors that affect H entry include a broad range of metallurgical, environmental and interface properties such as adsorption, surface segregation and surface films. Another recently recognized important parameter is the existence of recesses in the surfaces.[1-3] These can be pre-existing or produced during service by the occurrence of nonuniform (localized) corrosion processes. Research during this grant period focused on understanding how these parameters control hydrogen entry. The specific investigations included both aqueous and gas phase charging of hydrogen, utilizing primarily electrochemical techniques, in particular hydrogen permeation with the IPZ model,[4] and microscopic methods in the case of aqueous phase charging, and ultra high resolution scanning tunneling microscopy (STM) in the case of gas phase charging.

SUMMARY OF RESULTS

Significant results obtained on the Project in the period 10/1/90 to 9/30/93 include the following:

1. Following the procedure which enables application of the IPZ model to steady state permeation data, a study of the role of H_2S as an additive to aqueous electrolytes produced two significant results: (i) it demonstrated the applicability of the IPZ model as a diagnostic tool for better understanding how the various parameters promote or suppress hydrogen

entry, thereby hopefully encouraging others to use it for diagnosing the roles of the parameters determining hydrogen entry under other conditions, and (ii) the results indicate that H_2S additions to the electrolyte promote hydrogen entry by increasing the transfer coefficient of the proton discharge step and decreasing the hydrogen recombination rate constant. Though limited data were obtained, it is clear that these two parameters were affected by H_2S and that a more extensive permeation experiment would likely be conclusive on these two parameters and provide more detailed information. To put into perspective what the results obtained thus far indicate if taken at face value, is that the half dozen other mechanisms that can be envisioned or are already proposed in the literature are not applicable (for H_2S in acid solution) Only mechanisms based on the "bridging" concept first proposed by Kawashima, et. al. are consistent with the results.[5]

2a. Surface geometrical defects are in general known to account for inhomogeneous potential distribution over the surface. Thus, during spontaneous electrochemical processes, a potential gradient can be expected in cavities that are open to the electrolyte. What has been learned from experiments on the project is that the magnitude of the gradient is significant during cathodic or anodic polarization even for cavities of rather small aspect ratio when solid or gaseous reaction product form in the cavity. For the specific case of anodic polarization, either imposed or spontaneous, of steel and corrosion resistant alloys, the hydrogen evolution reaction sometimes occurs inside cavities as a result of the sign and magnitude of the potential gradient that can occur within the cavity.[1] This result demonstrates that surface geometry is a parameter that needs to be considered when studying the hydrogen entry issue, and is particularly significant because of its lack of recognition to the present time. Hydrogen permeation experiments are, in fact, confirming the expected, namely that some of the hydrogen formed inside the cavity enters the metal. This happens because recesses in the surface can promote hydrogen entry even under polarization conditions that do not permit proton discharge and hydrogen entry elsewhere on the surface.

b. The general phenomenon described above in a has some unique features when occurring in a grain boundary sensitized alloy. In this case the necessary potential conditions for hydrogen discharge and entry into the metal can develop with time even when there are no recesses in the original surface. Investigations on sensitized 430 stainless steel revealed that in the grain boundary grooves that formed by the Cr-depletion mechanism, the potential gradient inside the groove was sufficient to favor proton discharge and hydrogen entry into the steel within the groove.[3,6] We can learn from these results that it is important, indeed necessary, to consider the magnitude of the potential gradient within cracks, rather than solely considering the changes in solution composition within cracks, in order to obtain a more in-depth understanding of the conditions that produce crack propagation and the mechanism. The importance of this conclusion is highlighted by the recent literature findings for localized corrosion (crevice corrosion, pit growth and grain boundary corrosion) that steep potential gradients and the size of the active loop in the E-i curve within the cavity provide a more in-depth understanding and the framework for quantitative models that can successfully predict susceptibility, critical aspect ratio and current distribution within the cavity.

3. Scanning tunneling microscopy (STM) has been successfully used during the Grant period in studying the step preceding the actual entry (or absorption) of hydrogen into the metal. This atomic scale study of hydrogen adsorption was conducted using hydrogen gas as the hydrogen source. The vacuum environment and "model" substrates, e.g., silicon, provided experimental conditions for which adequate resolution was most readily achieved. Many features of the adsorption of hydrogen at room temperature have been observed including the initial adsorption sites (dimerised Si atoms), adsorption of hydrogen atoms as pairs, monohydride formation followed by dihydride formation and etching of Si atoms at higher fractional monolayer hydrogen coverages.[7] Atomic scale features of the desorption process with increasing temperature were also successfully monitored. Thus, the results show that STM can add to our understanding of hydrogen entry and are particularly encouraging (i)

when complimentary results are obtained by other methods which then enable more in depth STM studies and (ii) because of the capability of STM to probe the atomic scale.

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